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Introduction

The 37°C automated electrometer system has been completed and work is in progress on the 60°C system. UM interdigitated electrode test structures were assembled and placed under test. Post-implantation testing of Inter-Digitated Electrodes (IDEs) was completed for devices that had been implanted for up to several years.

Instrumentation

Two more banks of electrometers were assembled, de-bugged and calibrated this quarter. 3 foot long Teflon® insulated extension cables were added to these basic units to allow testing of the many existing assemblies in the 37°C incubators. Calibration of the systems revealed that the additional cables had sufficiently high shunt resistances to maintain the sensitivity of the electrometers. Also, motion artifacts from vibration were not a problem probably because of the averaging effects of the 100 second time constants of the current to voltage converters. Temperature controllers and readout interfaces for the computer acquisition of temperature were constructed and will be integrated into the system next quarter. Also, humidity monitoring will be added next quarter.

New Test Devices

Techniques for casting surface coating test devices were explored. This quarter we observed that some materials were collecting along the interfaces between layers of silicone used to construct surface coating test structures. These structures had previously been assembled using sheets of cast silicone that were glued to the backs of silicon test squares. The front of the test squares was coated with silicone except for the center that was left with a 0.5mm diameter opening for access to the saline solution. Apparently, the interface between the cast silicone and the front surface coatings was trapping species diffusing into the silicone. We suspect that the collecting material is silver from the reference electrode or the dissolved silver in the solution. While this probably does not affect the device performance, since control readings are as expected, it is an added variable. The goal of development of a casting technique is to avoid the interfaces that apparently develop during coating of cured silicone with additional silicone. A secondary goal is to improve our speed of assembly to allow more rapid results to be obtained for the surface coating portions of the study, particularly from the plasma and thermal deposition of silicone studies.

Several University of Michigan triple track devices provided by Mehmet Dokmedi were assembled and placed under soak test. Both devices failed rapidly, apparently due to assembly errors. One device exhibited extreme corrosion of the substrate apparently due to a connection of the bias to the substrate. This may have been due to a bond wire being located too close to the edge of the device. The second device also failed rapidly, but apparently the silicone was not fully cured as it had become soft and somewhat tacky. Review of the assembly procedures revealed that the post-cure cycle had been shortened. Whether or not this was a contributing factor will be explored next quarter.

New devices were constructed and were dry tested before immersion in saline to verify the assembly prior to testing. Resistivity readings were very low indicating that there may have been surface contamination between traces of the IDEs. There were no mistakes in assembly of these devices. Perhaps there was some residual metal between traces where the laser was used to remove defects that had shorted the traces during fabrication. As a test of this, new assemblies will be made next quarter where the pre-clean includes a soak in 10% HF to remove the surface layer of oxide and hopefully any residual metal.

Animal Testing

Subdural wire loops insulated with commercially available Teflon® coated wires have been implanted in animals for one year. Recent testing shows that resistances are holding at greater than $10^{14}\Omega$ for approximately 1cm of 2 or 3 mil diameter platinum wire that has been insulated with approximately 18μm of Teflon®. Subcutaneous triple track devices coated with Nusil MED4211 or Nusil CF20-2186 were re-tested after over one year of implantation and 5 volt bias. Readings from 3e11-1e13Ω were obtained for the MED4211 coated devices. While continuity measurements showed that connections had resistances over 50MΩ, it is unlikely that these interfered with the resistivity measurements. However, this needs to be verified by actually taking continuity measurements with the system. One of four 2186 coated samples was low impedance (<10e10Ω), but the remaining three exhibited resistances greater than 10e13Ω. While continuity measurements for the electrodes receiving the currents were normal, the bias connection exhibited greater than 50MΩ resistance. Again, this probably doesn't affect the measurement since it is in series with 10e13Ω test structures.

Two additional changes need to be accomplished with the portable animal tester - one is that there needs to be decades of bias range to allow testing of devices with lower resistances than 10e10Ω. Also, a new adapter for the subdural triple track devices needs to be assembled in preparation for testing those devices.

Vapor Phase Silicone Depositions

Progress on silicone vapor phase depositions is covered in a summary document presented at an ONR workshop earlier this year (*Silicones in Coatings II*, Orlando, Florida March 24-26, 1998). A new series of test devices will be fabricated next quarter using the thermal and plasma techniques for long term soak testing if the defect density is low enough.

Appendix

A.1 Preliminary Results

Proceedings From "Silicones in Coatings II", Orlando, Florida, 24-26 March 1998

APPENDIX A.1

Pyrolytic Chemical Vapour Deposition of Poly(organosiloxane) Thin Films

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Abstract

A pyrolytic chemical vapour deposition method was used to deposit silicone polymer thin films from the thermal decomposition of the cyclic tetramer, octamethylcyclotetrasiloxane, over a hot filament. High deposition rates (up to 2.5 μm/min) could be achieved. Fourier transform infrared spectroscopy verified that the deposited films had the same functional groups as a poly(dimethylsiloxane) standard, though with a measurably lower methyl concentration. X-ray photoelectron spectroscopy showed that a typical film had an elemental composition of C:Si:O / 1.5:1:1, confirming the loss of methyl groups. ^{29}Si NMR suggested the existence of Si-Si crosslinks in the thin film. The dependence of the growth rate on the filament temperature gave an apparent activation energy of 36.5 ± 4.1 kcal/mol.

Introduction

Silicone is a generic name for the class of polymers which consist of a repeating Si-O backbone with organic functional groups attached to the Si via Si-C bonds. The most common of these functional groups is methyl, resulting in the silicone, poly(dimethylsiloxane) or PDMS. Because of its excellent combination of properties, conventional crosslinked PDMS is used in a wide range of applications from the potting and encapsulation of electronics and electrical connections to medical implants such as heart valve poppets and intraocular lenses.[1] There has been considerable interest in extending these applications through the chemical vapour deposition of silicone thin films. Potential applications include biocompatible coatings for medical implants,[2] permselective membranes,[3] integrated optical devices,[4] dielectric films,[5] and abrasion and corrosion resistant coatings.[6] To date, all such efforts have focused on plasma enhanced CVD (PECVD) deposited films from a large variety of monomers such as hexamethyldisiloxane, tetramethylsilane, and octamethylcyclotetrasiloxane; these have all been extensively reviewed by Wróbel and Wertheimer.[7] A potential problem in the application of these films as dielectric layers, however, arises due to the high dielectric loss when compared to the conventional polymer as well as an aging effect upon exposure to the atmosphere. Both of these effects can be related to the high density of trapped radicals in plasma deposited materials. These defects can originate from electron impact fragmentation of gaseous reactants and from UV irradiation[8] ion bombardment of the surface.[9] A pyrolytic process, on the other hand, in which the growth precursors are thermally produced does not suffer from ion bombardment and UV irradiation and has been shown in the case of fluorocarbon polymer CVD to result in a lower density of dangling bonds.[10]

We present a pyrolytic process for the deposition of silicone thin films from the low-pressure thermolysis of octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, also known as D_4 from the commonly used nomenclature of D for $-(CH_3)_2SiO-$. D_4 is a monomer which is commonly used in the base catalyzed, liquid phase ring-opening polymerization to PDMS. In addition, D_4 melts at 17 °C and hence is a liquid at standard conditions with a reasonable vapour pressure.

Experimental

In our experiments, approximately 2 sccm of D_4 was vapourised through the reactor chamber (Figure 1) by mildly heating a Pyrex container attached to a valve on the chamber. Pressure was maintained at 0.6 torr by adjusting a throttle valve in the reactor outlet. A 1 mm diameter tantalum wire was resistively heated to between 260 and 530°C for these experiments. The substrate was a 2" Si wafer sitting 11 mm away on a water cooled stage; the temperature as measured by a thermocouple on the backside of the wafer was 20 ± 3°C. The growth rate in the center of the substrate varied from 2.5×10^4 to 5 Å/min depending on the filament temperature. By comparison, the maximum deposition rates reported for the plasma polymerization of hexamethyldisiloxane varied from 0.5 $\mu g\ cm^{-2}\ s^{-1}$ for capacitively coupled discharges[11] to 2.6 $\mu g\ cm^{-2}\ s^{-1}$ for microwave discharges,[12] which translates to linear growth rates of about 3×10^3 and 1.6×10^4 Å/min, respectively.

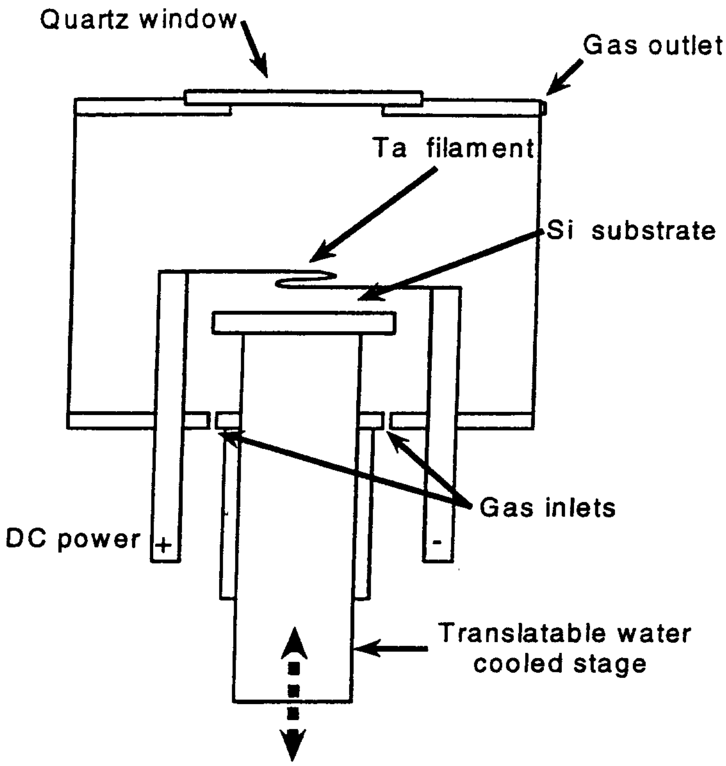

Figure 1: Schematic of pyrolytic CVD reactor

Fourier Transform Infrared (FTIR) Spectroscopy

A comparison of the typical Fourier transform infrared spectra of a CVD thin film produced at a filament temperature ($T_{filament}$) of 415 ± 5°C versus that for a viscous liquid PDMS standard (Aldrich Chemical, secondary standard) is shown in Figure 2. A qualitative analysis of the spectra indicates that the sample and the standard have absorbance peaks at identical wavelengths and hence identical IR active functional groups. In order to permit semi-quantitative analysis, the spectra are shown in normalized absorbance units. The main feature to note in this case is the marked difference in relative intensity between the CVD film and the PDMS standard at 2964 cm^{-1}, 1410 cm^{-1}, and 702 cm^{-1}. The peaks at 2964 cm^{-1} and 2906 cm^{-1} are due to the asymmetric and symmetric C-H methyl stretches, respectively, while the peak at 1410 cm^{-1} is the result of the C-H methyl bending modes.[13] This implies that the CVD film is deficient in methyl substituents as compared to the PDMS standard. We can also rule out the loss of sp^3-CH_3 absorption intensity due to any C-C crosslinking since such a rearrangement would result in the appearance of new peaks in the C-H stretch region at a lower wavenumber corresponding to sp^3-CH_2. The peak at 702 cm^{-1} is in a region which is typically assigned to Si-C stretches.[14]

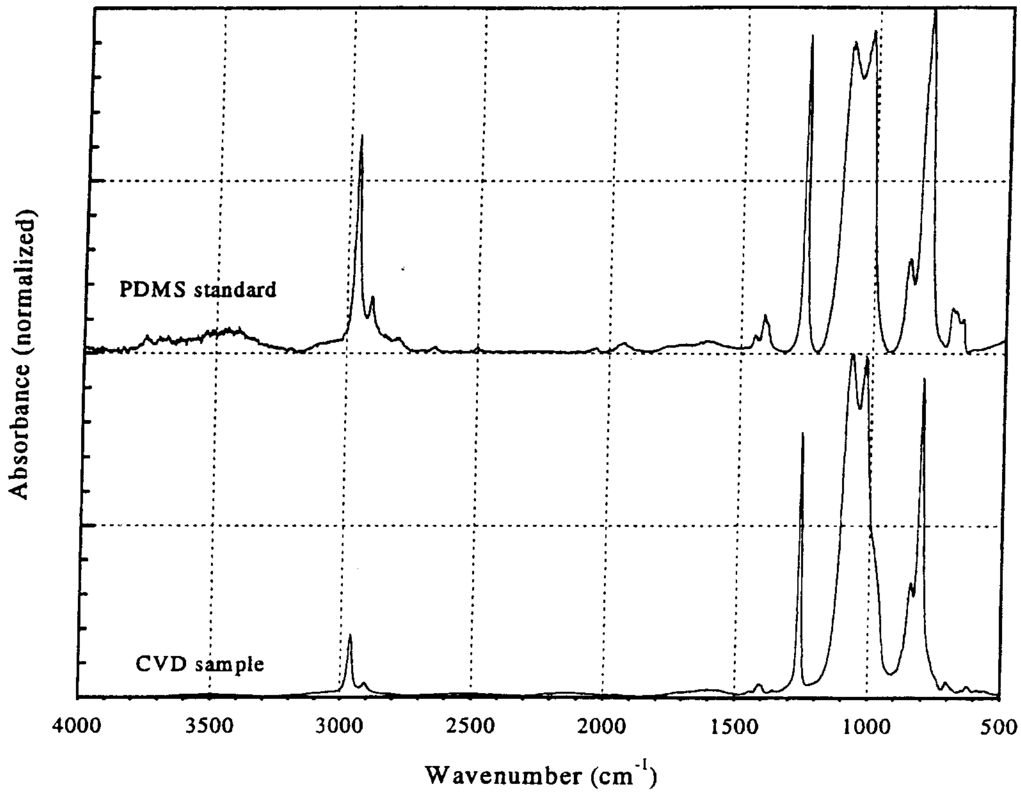

Figure 2: Comparison of FTIR spectra of a 6.9 μm thick pyrolytic CVD thin film with a poly(dimethylsiloxane) standard

X-Ray Photoelectron Spectroscopy (XPS)

Further analysis was carried out by X-ray photoelectron spectroscopy (XPS). Survey scans were conducted on several CVD thin films as well as the PDMS standard to determine the relative elemental composition. By assuming that the PDMS standard has the ideal elemental composition of C_2SiO and adjusting the instrument sensitivity factors for the O 1s, C1s, and Si 2p peaks to reflect this, the composition of the $T_{filament}$ = 415°C sample was determined to be $C_{1.53}Si_{1.00}O_{1.00}$ which confirms the loss of methyl substituents shown by FTIR spectroscopy. It further shows that the Si-O backbone is left intact by the deposition process. The films deposited at other filament temperatures demonstrated similar compositions. The loss of methyl groups may lead to crosslinking in the films. To test this hypothesis, solubility tests on as deposited thin films were conducted in benzene, toluene, and a mixture of xylene isomers. In all cases, the weight loss was minimal, being less than 10% and limited by the resolution and accuracy of the balance.

^{29}Si Nuclear Magnetic Resonance (NMR) Spectroscopy

A home built nuclear magnetic resonance spectrometer[15] with a ^{29}Si resonance frequency of 53.64 MHz was used to probe the chemical nature of the silicon nuclei in the pyrolytic films through cross-polarization / magic-angle spinning (CP / MAS) solid state ^{29}Si NMR. Two films were deposited at a pressure of 0.6 torr, a filament power of 120W, and a filament-to-substrate distance of 10.5 mm for two hours each in order to accumulate enough material for analysis. Approximately 60 milligrams were scraped off of the silicon substrates, mixed with alumina as a filler, and packed into a rotor which was spun at 3.5 kHz. The spectrum shown in Figure 3 was collected in a Chemagnetics 7.5 mm, double resonance, MAS probe using a 7 μs 90° pulse followed by 3 ms cross polarization contact time. A total of 512 signal averages with a 20 μs dwell time and a 20 s recycle delay were used. Note that unlike direct excitation NMR, the area under the peaks in CP spectra cannot be directly compared to give quantitative relative concentration information.

A listing of some of the many possible functional groups and their chemical shifts from the literature is shown in Table 1. The two main peaks in our spectrum occur at -8 and -19 ppm. The peak at -19 ppm corresponds to the Si in a dimethylsiloxane unit. As one can see from the spectra for pure D_4 and the PDMS secondary standard in Figures 4 and 5, respectively, this peak can shift from -18 ppm to -23 ppm. As in the published spectra for PP films, this peak is the most prominent. In PP films from D_4, there are two other significant peaks at ~10 ppm and ~ -60 ppm corresponding to $(CH_3)_3Si–O–$ and $(CH_3)Si–(O)_3–$ groups,

Table 1: Literature values for various functional groups and their ^{29}Si NMR chemical shifts relative to TMS

Chemical group	Chemical shift (ppm)	References
$(CH_3)_3Si{-}O{-}$	+6 to +11	Assink *et al.*,[16] Engelhardt *et al.*[17]
$(CH_3)_4Si$	0	zero reference
$-O-(CH_3)_2Si-O-$	-18 to -23	Assink *et al.*,[16] Engelhardt *et al.*[17]
$-O-(CH_3)Si(-O-)-O-$	-55 to -68	Assink *et al.*,[16] Horn *et al.*[18]
$-O-Si(-O-)(-O-)-O-$	-99 to -109	Assink *et al.*,[16] Tajima *et al.*[19]
$(CH_3)_2HSi-O-$	-5	Assink *et al.*,[16] Mileshkevich *et al.*[20]
$-O-(CH_3)HSi-O-$	-33 to -39	Assink *et al.*,[16] Horn *et al.*[18]

respectively; see Figure 6.[19] Both of these types of Si are present in our films as well but at barely detectable levels.

The peak in our spectrum at -8 ppm is in the range typically assigned to a terminal $(CH_3)_2HSi{-}O{-}$ group or a siloxane unit with a vinyl group attached. The latter has been ruled out by the lack of CH_2 absorptions in the IR spectra while the former was checked by a CP contact time experiment in which the effect of varying the contact time on the relative intensity of the two main peaks was monitored. Because the peaks did not display different responses as the contact time was increased, the -8 ppm peak is not likely to be from any functional groups with Si-H bonds. Also, considering the loss of methyl groups indicated by the IR and XPS spectroscopies, it seems unlikely that a significant concentration of

$(CH_3)_2HSi$– groups could be present without some detectable levels of –O–$(CH_3)HSi$–O– (~ -36 ppm) as well.

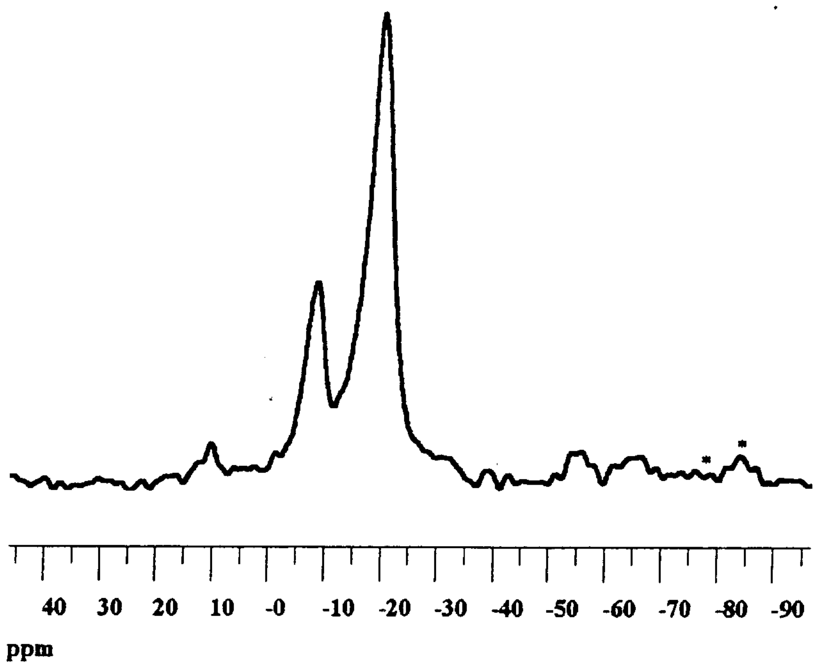

Figure 3: ^{29}Si NMR spectrum of an as deposited pyrolytic PDMS film

(* = spinning side bands)

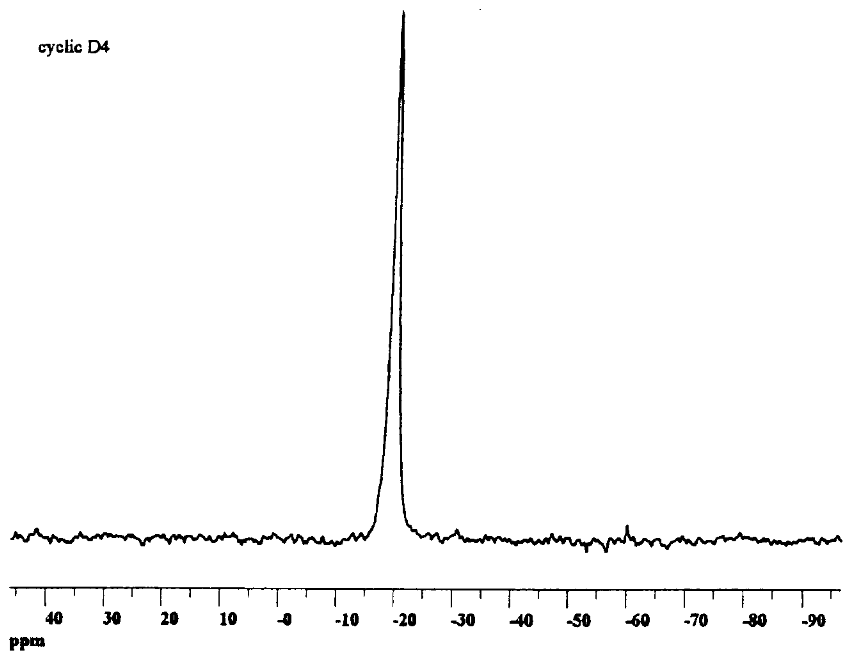

Figure 4: ^{29}Si NMR of octamethylcyclotetrasiloxane (D_4)

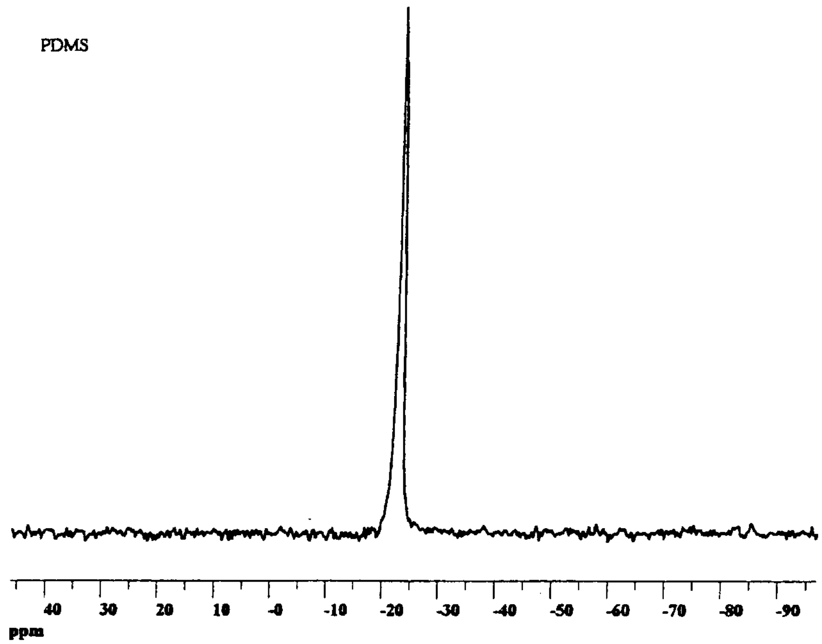

Figure 5: ^{29}Si NMR of polydimethylsiloxane (PDMS) secondary standard

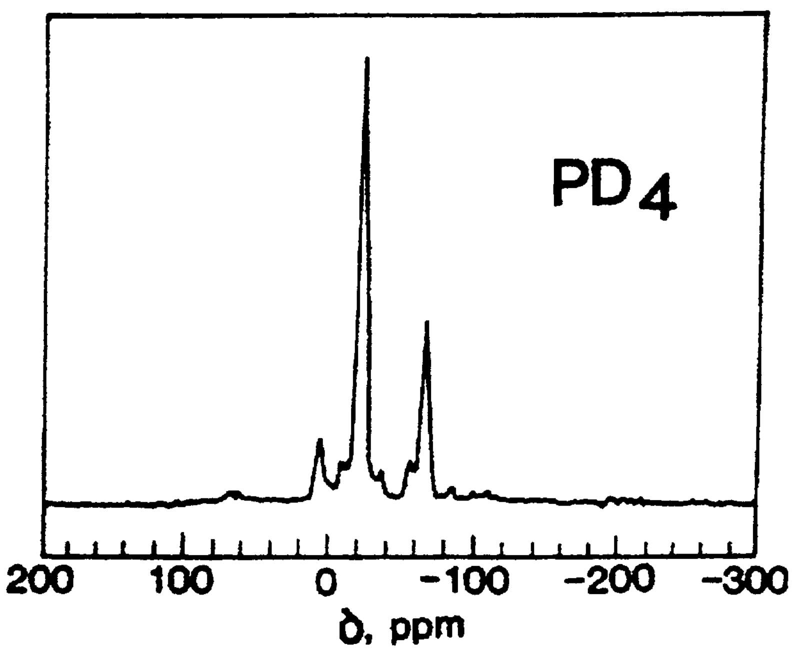

Figure 6: ^{29}Si NMR spectrum for plasma polymerized D_4 film

From I. Tajima, and M. Yamamoto, *J. Polym. Sci. Polym. Chem.*, **25**, 1737 (1987)

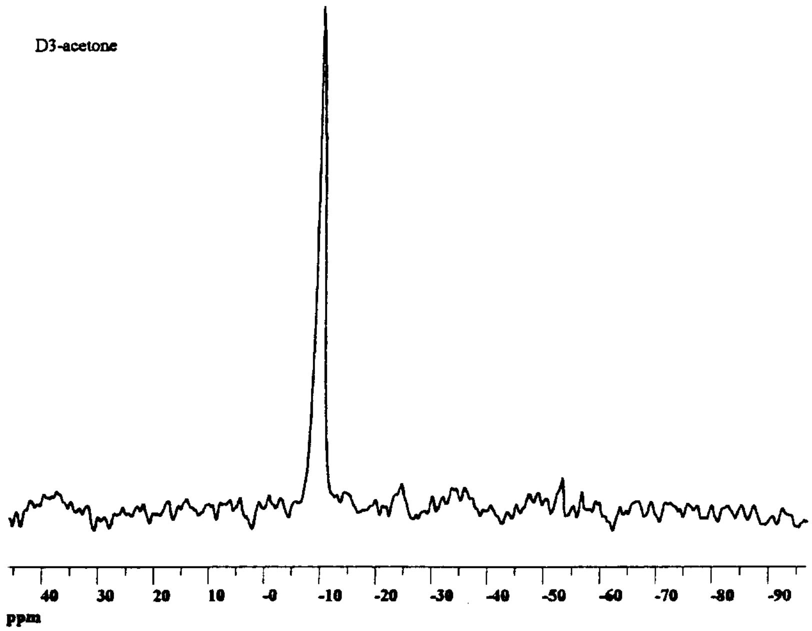

Figure 7: ^{29}Si NMR of hexamethylcyclotrisiloxane (D_3)

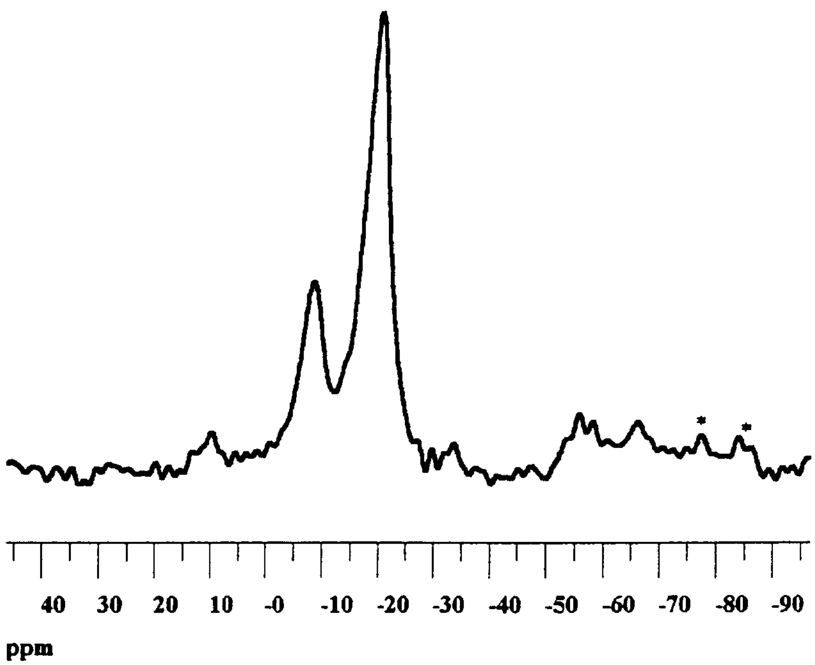

Figure 8: ^{29}Si NMR spectrum of the annealed pyrolytic PDMS sample

(* = spinning side bands)

Another possible source of a chemical shift in the range between 0 and -10 ppm is from D_3, the solid cyclic trimer, which we determined has a shift of -9 ppm. The spectrum for D_3 dissolved in acetone is shown in Figure 7. To check for the presence of D_3, the pyrolytic sample was heated to 135 °C in air for 30 minutes. Since D_3 has a boiling point of ~134 °C, such a heat treatment should remove most if not all traces of the trimer. Because the sample was mixed with alumina to pack the rotor, no significance could be attributed to the slight weight loss in the sample upon cooling. The NMR spectrum in Figure 8 shows that the heat treatment had no effect on the sample.

Yet another possible source for the signal at -8 ppm is the presence of **(1)** $-O-(CH_3)_2Si-Si(CH_3)_2-O-$ or **(2)** $-(O)_2-(CH_3)Si-Si(CH_3)-(O)_2-$ groups. The existence of such Si-Si crosslinks is in agreement with the methyl loss shown by FTIR and XPS and does not contradict the ^{29}Si NMR data. Furthermore, because the high resolution Si 2p XPS spectra have indicated that no significant concentration of any oxidation states besides Si^{2+} are present, we can very likely rule out **(1)**, the head-to-tail dimethylsiloxane unit, which only has single oxidation state Si's. However, since no literature references for the chemical shift of **(2)** have been found, this assignment is tentative.

Growth Rate

In order to better understand the kinetics of this process, the growth rate was measured at several filament temperatures and the results plotted in Arrhenius form. For films under approximately a micron in thickness, the deposition rate was measured by ellipsometry. Thicker films were measured by scratching the film and using a stylus profilometer. Figure 9 is a graph of the natural log of the growth rate versus the reciprocal of the filament temperature. A linear fit to the data is shown and yields an activation energy of 36.5 ± 4.1 kcal/mol. This activation energy differs from the value reported for the gaseous pyrolysis of D_4 at similar pressures (0.5 - 13.5 torr). The early stages of D_4 pyrolysis (<4% decomposition) had an activation energy of 72 ± 2 kcal/mol over the temperature range 493 - 569°C.[21] These temperatures are high compared to the filament temperatures used for pyrolytic CVD in this work (270 - 530 °C). However, the pyrolysis kinetics were also found to be sensitive to trace oxygen contamination.

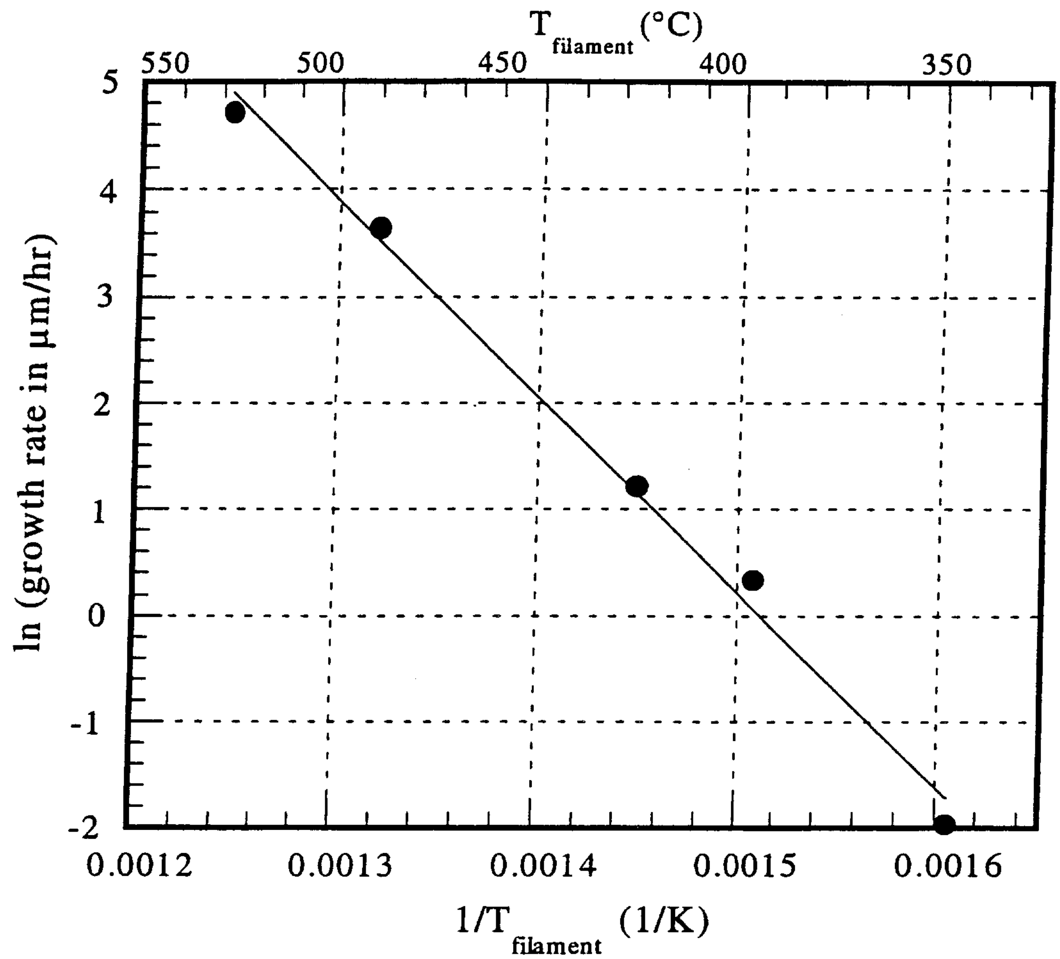

Figure 9 : Arrhenius plot for pyrolytic CVD at 0.6 torr

Growth Mechanism

A possible polymerization mechanism is suggested by the activation energy (42 ± 3 kcal/mol) for the thermal degradation of a number of linear PDMS films in a vacuum.[22] Based on the observed temperature invariance of the equilibrium ratio of oligomers and polymers in the liquid phase ring-opening polymerization of PDMS, it has also been shown that $\Delta H_{polymerization} \approx 0$.[23] The nearly equal activation energies for the polymerization and degradation processes could be explained if we hypothesize a similar gas phase ring-opening process with a similar near zero enthalpy change.

Another mechanism is suggested by the stable products of D_4 pyrolysis, D_3 and D_5.[21] The proposed pyrolysis mechanism involves the decomposition of D_4 to D_3 and an intermediate, D_1 (dimethylsilanone), followed by the reaction of D_1 with D_4 to give D_5 as the second stable product. The decomposition of D_4 may involve the formation of a bicyclic transition state, accounting for the predominate cleavage of the Si-O bond as compared to the weaker Si-C bond.[24] This stabilized transition state could explain the growth of larger siloxane rings and chains.

Conclusions

A thermally activated process for the CVD of silicone-like films, which have a similar structure to that of poly(dimethylsiloxane) as confirmed by FTIR spectroscopy, has been demonstrated. In contrast to PECVD, the pyrolytic CVD process does not involve any ion bombardment or UV irradiation, thus eliminating the possibility of related atomic rearrangements and defects. The ability to grow fluorocarbon[10] and silicone thin films by pyrolytic CVD reveals that ion bombardment, which is often cited in discussions of PECVD mechanisms as being essential to the creation of active sites for film growth,[7] is in fact not necessary for the deposition of these materials. In addition, very high silicone growth rates have been achieved by pyrolytic CVD. We anticipate that changes in reactor conditions such as pressure, filament-to-substrate standoff, flow rate, and substrate temperature will result in even higher rates.

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